

# Doping and disorder in the $\text{Co}_2\text{MnAl}$ and $\text{Co}_2\text{MnGa}$ half-metallic Heusler alloys

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We expand our study on the full-Heusler compounds [I. Galanakis *et al.*, Appl. Phys. Lett. **89**, 042502 (2006)] to cover also the case of doping and disorder in the case of  $\text{Co}_2\text{MnAl}$  and  $\text{Co}_2\text{MnGa}$  half-metallic Heusler alloys. These alloys present a region of very small minority density of states instead of a real gap. Electronic structure calculations reveal that doping with Fe and Cr in the case of  $\text{Co}_2\text{MnAl}$  retains the half-metallicity contrary to the  $\text{Co}_2\text{MnGa}$  compound. Cr impurities present an unusual behavior and the spin moment of the Cr impurity scales almost linearly with the concentration of Cr atoms contrary to the  $\text{Co}_2\text{MnZ}$  ( $Z = \text{Si, Ge, Sn}$ ) where it was almost constant. Half-metallicity is no more preserved for both  $\text{Co}_2\text{MnAl}$  and  $\text{Co}_2\text{MnGa}$  alloys when disorder occurs and there is either excess of Mn or *sp* atoms.

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Research on half-metallic ferromagnets is rapidly growing since its prediction for  $\text{NiMnSb}$  in 1983 by de Groot and his collaborators.<sup>1</sup> The driving force of the interest in these materials is their potential applications in magnetoelectronic applications.<sup>2,3,4,5,6</sup> Electronic structure calculations have played a central role on the study of these materials. Several new half-metallic ferromagnetic materials and their properties have been initially predicted by theoretical ab-initio calculations and later verified by experiments. Among the half-metallic materials, intermetallic Heusler alloys have attracted considerable attention due their easy growth and the high Curie temperatures.<sup>7,8</sup>

The full-Heusler compounds containing Co and Mn are of particular interest for spintronics since they combine high Curie temperatures and coherent growth on top of semiconductors (they consist of four f.c.c. sublattices with each one occupied by a single chemical element). To precisely control the properties of these compounds we have to study effects susceptible of inducing states within the minority spin gap and thus destroy the half-metallicity. States at the interfaces of these compounds with semiconductors<sup>9</sup> as well as temperature driven excitations<sup>10,11,12</sup> seem to destroy half-metallicity. In addition to interface states and temperature, the third main effect which can destroy half-metallicity is the appearance of defects and disorder.

In a recent paper<sup>13</sup> we studied the effect of doping and disorder on the magnetic properties of the  $\text{Co}_2\text{MnSi}$ ,  $\text{Co}_2\text{MnGe}$ ,  $\text{Co}_2\text{MnSn}$  full-Heusler alloys. Doping simulated by the substitution of Cr and Fe for Mn in these alloys overall keeps the half-metallicity. The effect of doping depended clearly on the position of the Fermi level, having the largest one in the case of  $\text{Co}_2\text{MnSi}$  where the

Fermi level is near the edge of the minority-spin gap. On the other hand disorder, simulated either by excess of Mn atoms at the D site occupied in the perfect compound by the *sp* atoms or *vice versa*, was found to be more important for the heavy *sp* atoms like Sn but in general the half-metallicity was almost preserved.

In this manuscript we expand our theoretical work to include also the case of  $\text{Co}_2\text{MnAl}$  and  $\text{Co}_2\text{MnGa}$  compounds which have one valence electron less than that of the previous ones. Doping by electrons simulated by partial substitution of Fe for Mn in the unit cell has little effect on the gap-properties while Cr impurities, corresponding to hole doping, exhibit a more unusual behavior. A high degree of spin-polarization at the Fermi level is overall preserved but contrary to what happens for the Si, Ge and Sn compounds and to the Fe-doping case, Cr impurities present a very small spin moment for small concentrations which increases with the concentration. In the last part of our study we concentrate on the case of disorder which is shown to severely affect the half-metallicity contrary to the  $\text{Co}_2\text{MnZ}$  ( $Z = \text{Si, Ge, Sn}$ ) alloys. The electronic structure calculations are performed using the full-potential nonorthogonal local-orbital minimum-basis band structure scheme (FPLO).<sup>14</sup>

Before presenting our results we have drawn in Fig. 1 the atom-resolved DOS for the  $\text{Co}_2\text{MnZ}$  compounds. On the left column are the case with Z a *sp* element belonging to the IIIB column of the periodic table (Al and Ga) and in the right column the case of IVB elements (Si, Ge and Sn). The extra electron in the latter case occupies majority states leading to an increase of the exchange splitting between the occupied majority and the unoccupied minority states and thus to larger gap-width for the

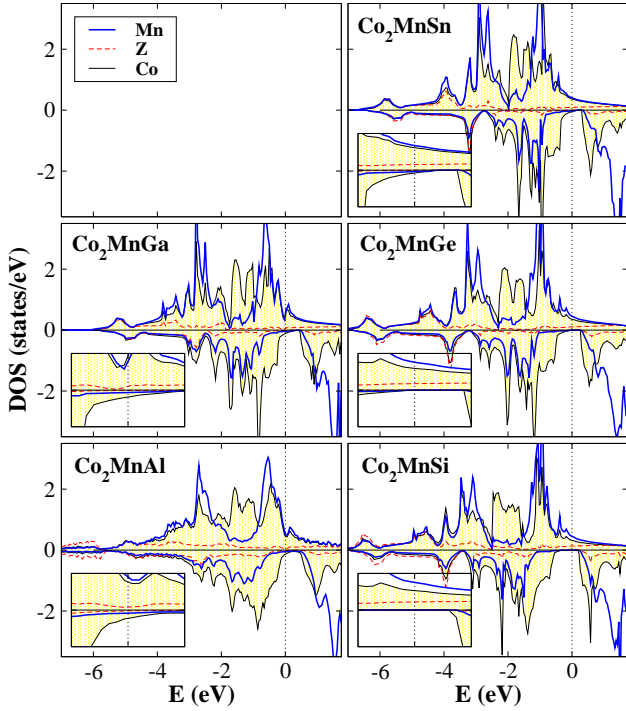


FIG. 1: (Color online) Atom-resolved density of states (DOS) for the  $\text{Co}_2\text{MnZ}$  compounds, where Z is Al, Ga, Si, Ge, and Sn. We have set the Fermi level as the zero of the Energy axis. In the onsets we have blown up the region around the Fermi level. Note that positive values of DOS refer to the majority-spin electrons and negative values to the minority-spin electrons.

Si-, Ge- and Sn-based compounds. In the case of Al- and Ga-based alloys the bonding and antibonding minority d-hybrids almost overlap and the gap is substituted by a region of very small minority density of states (DOS); we will call it a pseudogap. In all cases the Fermi level falls within the gap or the pseudogap and an almost perfect spin-polarization at the Fermi level is preserved.

Firstly we will study the doping in these compounds. We substitute either Fe or Cr for Mn to simulate the doping by electrons and holes, respectively. We study the cases of moderate doping by substituting 5%, 10% and 20% of the Mn atoms. In our calculations the use of coherent potential approximation ensures doping in a random way. In Fig. 2 we present the total density of states (DOS) for the  $\text{Co}_2\text{Mn}_{1-x}(\text{Fe or Cr})_x\text{Al}$  alloys to compare to the perfect  $\text{Co}_2\text{MnAl}$  alloys and in Table I we have gathered the total and atom-resolved spin moments for both Al- and Ga-based alloys. Note that in the figure we have blown up in the onsets the region around the Fermi level where the gap exists.

Fig. 2 confirms the discussion in Ref. 7 that the gap is created between states located exclusively at the Co sites. As was the case also for the compounds in Ref. 13 the majority-spin occupied states form a common Mn-Co band while the occupied minority states are mainly located at the Co sites and minority unoccupied at the Mn

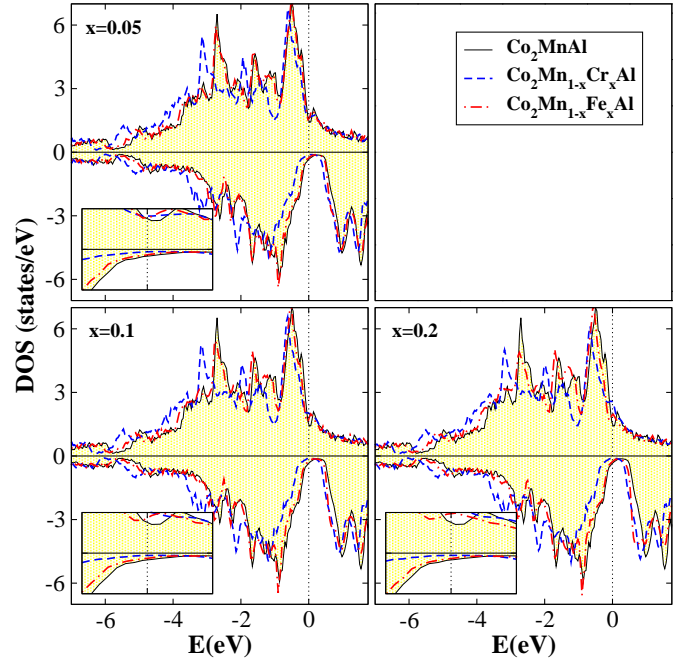


FIG. 2: (Color online) Spin-resolved DOS for the case of  $\text{Co}_2\text{Mn}_{1-x}\text{Cr}_x\text{Al}$  and  $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Al}$  for three values of the doping concentration  $x$ . DOS's are compared to the one of the undoped  $\text{Co}_2\text{MnAl}$  alloy. Details as in Fig. 1.

sites. Doping the perfect ordered alloy with Fe has only a marginal effect on the total DOS compared to the more significant effects of the doping with Cr. In the latter case it seems that Cr-doping slightly opens the pseudogap and pushes both the majority and minority occupied bands lower in energy. This behavior upon Cr doping is also reflected on the spin moment of the Cr impurity atoms as we will discuss latter in the manuscript and is in contrast to what happens upon Cr-doping for the  $\text{Co}_2\text{MnSi}$  compound presented in Ref. 13 where the DOS scarcely changed. The important detail is what happens around the Fermi level and in what extent is the gap in the minority band affected by the doping. So now we will concentrate only at the enlarged regions around the Fermi level. The blue dashed lines represent the Cr-doping while the red dash-dotted lines are the Fe-doped alloys. The situation is reversed with respect to the  $\text{Co}_2\text{MnSi}$  compound, Cr-doping has significant effects to the pseudogap. Its width is larger with respect to the perfect compound and becomes slightly narrower as the degree of the doping increases. We will discuss this behavior in detail later in the text. Fe-doping on the other hand almost does not change the DOS around the Fermi level. The extra-electrons occupy high-energy lying antibonding majority states but since  $\text{Co}_2\text{MnAl}$  has one valence electron less than  $\text{Co}_2\text{MnSi}$  half-metallicity remains energetically favorable and no important changes occur upon Fe-doping and further substitution of Fe for Mn should retain the half-metallicity even for the  $\text{Co}_2\text{FeAl}$  compound contrary to the  $\text{Co}_2\text{FeSi}$  compound which is not half-metallic.<sup>15</sup>

TABLE I: Total and atom-resolved spin magnetic moments for the case of Fe and Cr doping of the Mn site in  $\mu_B$ . The total moment in the cell is the sum of the atomic ones multiplied by the concentration of this chemical element. Note that for Cr, Mn and Fe we have scaled the spin moments to one atom and that for Co we give the sum of the moments of both atoms.

	Total	Co	Mn	Cr	sp	Total	Co	Mn	Fe	sp		Total	Co	Mn	Cr	sp	Total	Co	Mn	Fe	sp
$x$	$\text{Co}_2\text{Mn}_{1-x}\text{Cr}_x\text{Al}$					$\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Al}$					$x$	$\text{Co}_2\text{Mn}_{1-x}\text{Cr}_x\text{Si}$					$\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$				
0.00	4.04	1.36	2.82		-0.14	4.04	1.36	2.82		-0.14	0.00	5.00	1.96	3.13		-0.09	5.00	1.96	3.13		-0.09
0.05	3.95	1.49	2.69	0.34	-0.13	4.06	1.44	2.76	2.78	-0.13	0.05	4.95	1.97	3.12	2.06	-0.09	5.05	2.02	3.13	2.87	-0.09
0.10	3.90	1.51	2.71	0.62	-0.11	4.11	1.49	2.76	2.78	-0.13	0.10	4.90	1.97	3.12	2.07	-0.09	5.09	2.06	3.17	2.85	-0.08
0.20	3.80	1.54	2.74	0.91	-0.11	4.21	1.58	2.76	2.79	-0.13	0.20	4.80	1.97	3.12	2.09	-0.08	5.14	2.13	3.16	2.82	-0.08
$x$	$\text{Co}_2\text{Mn}_{1-x}\text{Cr}_x\text{Ga}$					$\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Ga}$					$x$	$\text{Co}_2\text{Mn}_{1-x}\text{Cr}_x\text{Ge}$					$\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Ge}$				
0.00	4.09	1.30	2.88		-0.10	4.09	1.30	2.88		-0.10	0.00	5.00	1.87	3.20		-0.06	5.00	1.87	3.20		-0.06
0.05	4.05	1.36	2.93	0.20	-0.10	4.15	1.36	2.90	2.76	-0.10	0.05	4.95	1.86	3.21	2.05	-0.06	5.05	1.91	3.22	2.88	-0.06
0.10	4.00	1.39	2.94	0.55	-0.10	4.20	1.41	2.90	2.76	-0.10	0.10	4.90	1.86	3.22	2.07	-0.06	5.10	1.96	3.23	2.88	-0.06
0.20	3.88	1.42	2.97	0.91	-0.09	4.30	1.52	2.92	2.77	-0.10	0.20	4.80	1.86	3.22	2.10	-0.06	5.19	2.06	3.26	2.89	-0.05

TABLE II: Total and atom-resolved spin magnetic moments for the case of Cr doping of the Mn site for both Al- and Si-based compounds in  $\mu_B$ . Details as in Table I.

$x$	$\text{Co}_2\text{Mn}_{1-x}\text{Cr}_x\text{Al}$					$\text{Co}_2\text{Mn}_{1-x}\text{Cr}_x\text{Si}$				
	Total	Co	Mn	Cr	sp	Total	Co	Mn	Cr	sp
0.00	4.04	1.36	2.82		-0.14	5.00	1.96	3.13		-0.09
0.10	3.90	1.51	2.71	0.62	-0.11	4.90	1.97	3.12	2.07	-0.09
0.20	3.80	1.54	2.74	0.91	-0.11	4.80	1.97	3.12	2.09	-0.08
0.30	3.70	1.55	2.76	1.09	-0.10	4.70	1.96	3.12	2.11	-0.08
0.40	3.60	1.55	2.77	1.20	-0.10	4.60	1.95	3.12	2.12	-0.08
0.50	3.50	1.55	2.78	1.29	-0.09	4.50	1.94	3.13	2.14	-0.07
0.60	3.40	1.54	2.79	1.37	-0.09	4.40	1.93	3.13	2.15	-0.07
0.70	3.30	1.54	2.80	1.43	-0.08	4.30	1.92	3.13	2.16	-0.07
0.80	3.20	1.53	2.83	1.48	-0.08	4.20	1.91	3.13	2.17	-0.07
0.90	3.10	1.51	2.84	1.53	-0.07	4.10	1.90	3.12	2.17	-0.07
1.00	3.00	1.46		1.63	-0.09	4.00	1.89		2.17	-0.06

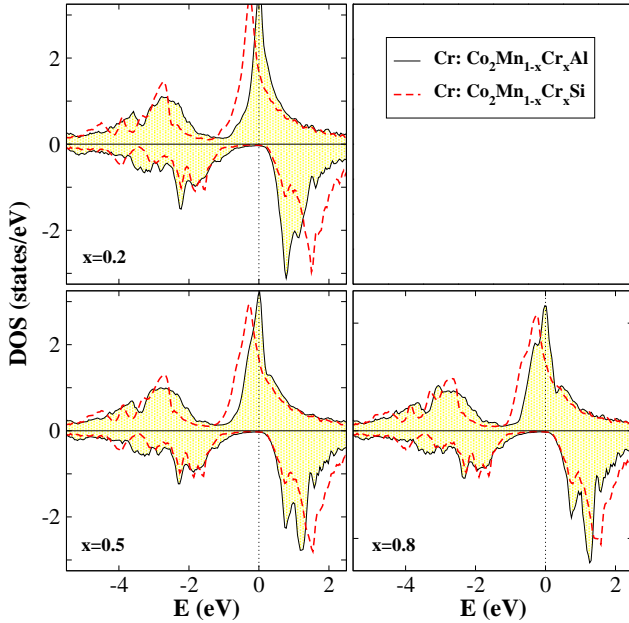


FIG. 3: (Color online) Cr-resolved DOS in the case of the  $\text{Co}_2\text{Mn}_{1-x}\text{Cr}_x\text{Al}$  and  $\text{Co}_2\text{Mn}_{1-x}\text{Cr}_x\text{Si}$  compounds for three different values of the concentration  $x$ . Details as in Fig. 1.

In Table I we have gathered the spin magnetic moments for all cases under study. For perfect half-metals the total spin moment  $M_t$  follows the Slater-Pauling (SP) behavior being the number of the valence electrons in the unit cell minus 24.<sup>7</sup> The perfect  $\text{Co}_2\text{MnAl}$  and  $\text{Co}_2\text{MnGa}$  compounds have total spin moments slightly larger than the ideal  $4 \mu_B$  predicted by the SP rule while the total spin moments of the Si- and Ge-based alloys are exactly  $5 \mu_B$  as predicted by the SP rule. In the case of the chemically disordered compounds, doping by 5%, 10% or 20% of Cr (or Fe) atoms, means that the mean value of the total number of valence electrons in the unit cell is decreased (or increased respectively) by 0.05, 0.10 and 0.20 electrons, respectively. The half-metallicity retains only when we dope  $\text{Co}_2\text{MnAl}$ . On the other hand for the  $\text{Co}_2\text{MnGa}$  compound the Fermi level is deeper in energy as shown in Fig. 1 and both perfect and disordered compounds are not half-metallic.

The atom-resolved spin moments in Table I present a striking peculiarity when we dope with Cr. In the case of  $\text{Co}_2\text{MnSi}$  (or Ge) compounds, the Cr impurities have a moment of slightly larger than  $2 \mu_B$  independent of the degree of doping. Similarly Fe impurities have a spin moment of around  $2.8 \mu_B$ . In the case of the  $\text{Co}_2\text{MnAl}$  and  $\text{Co}_2\text{MnGa}$  compounds Fe impurities have also a large spin moment of the same order of magnitude. But Cr impurities have a very small spin moment ( $0.3 \mu_B$  for the Al compounds and  $0.2 \mu_B$  for the Ga compound) for the case of 5% doping. Substituting 10% or 20% of Cr for the Mn atoms leads to a doubling or tripling, respectively, of the Cr-impurity spin moment. To elucidate this behavior, we have performed calculations for both  $\text{Co}_2[\text{Mn}_{1-x}\text{Cr}_x]\text{Al}$  and  $\text{Co}_2[\text{Mn}_{1-x}\text{Cr}_x]\text{Si}$  compounds for values of  $x$  ranging from 0 to 1 and we have gathered the atom-resolved spin moment in Table II and in Fig. 3 we have drawn the Cr-resolved DOS for three values of  $x$ . In the case of Si-compounds Cr-impurities spin moment is almost constant irrespectively of the concentration. On the other hand for the Al-compounds the spin moment of the Cr-impurities increases with the concentration of the Cr atoms. Fig. 3 explains this phenomenon. In the case of the Si-compounds the Fermi level falls after the

TABLE III: Total and atom-resolved spin magnetic moments for the case of excess of Mn ( $x$  positive) or  $sp$  atoms ( $x$  negative) atoms. In the second column the ideal total spin moment if the compound was half-metallic. Details as in Table I.

$x$	Ideal	$\text{Co}_2\text{Mn}_{1+x}\text{Al}_{1-x}$				$\text{Co}_2\text{Mn}_{1+x}\text{Ga}_{1-x}$			
		Total	Co	Mn	Al	Total	Co	Mn	Ga
-0.20	3.40	3.26	1.09	2.89	-0.12	3.40	1.11	3.00	-0.09
-0.15	3.55	3.45	1.15	2.87	-0.12	3.57	1.15	2.98	-0.10
-0.10	3.70	3.64	1.22	2.84	-0.13	3.74	1.21	2.94	-0.10
-0.05	3.85	3.83	1.29	2.83	-0.13	3.92	1.25	2.93	-0.10
0.00	4.00	4.04	1.36	2.82	-0.14	4.09	1.31	2.88	-0.10
0.05	4.15	4.22	1.40	2.81	-0.14	4.29	1.36	2.89	-0.11
0.10	4.30	4.40	1.44	2.81	-0.14	4.48	1.40	2.88	-0.11
0.15	4.45	4.60	1.49	2.81	-0.14	4.66	1.45	2.88	-0.11
0.20	4.60	4.80	1.54	2.81	-0.15	4.85	1.50	2.87	-0.11

majority peak and upon doping the relative position of the Fermi level does not change. This peak comes from the  $d$ -electrons of the Cr containing also the double degenerated  $e_g$  and triple degenerated  $t_{2g}$   $d$ -electrons. In the case of the Al-compounds the Fermi level is pinned exactly at the peak of the  $e_g$  electrons which are more localized and as we dope the compounds we change slightly the Coulomb repulsion and the exchange splitting and the triple degenerated  $t_{2g}$  electrons, which spread over a wider energy region, move lower in energy creating also the shoulder presented for  $x = 0.8$ .

In the last part of our study we study the effect of disorder. We either create an excess of the Mn or the  $sp$  atoms. In Table III we have gathered the total and

atomic spin moments for all cases under study. Substituting 5%, 10%, 15% or 20% of the Mn atoms by the Al or Ga ones, corresponding to the negative values of  $x$  in the table, results in a decrease of 0.15, 0.30, 0.45 and 0.60 of the total number of valence electrons in the cell, while the inverse procedure results to a similar increase of the mean value of the number of valence electrons. Contrary to the Si, Ge and Sn compounds presented in Ref. 13 which retained the perfect half-metallicity, the Al- and Ga-based compounds are no more half-metallic. In the case of the Si and related compounds disorder induced states at the edges of the gap keeping the half-metallic character but this is no more the case for the Al and Ga compounds where no real gap exists.

We have studied the effect of doping and disorder on the magnetic properties of the  $\text{Co}_2\text{MnAl}$  and  $\text{Co}_2\text{MnGa}$  full-Heusler alloys. These compounds present a region of low minority density of states instead of a real gap. Doping simulated by the substitution of Cr and Fe for Mn overall keeps the half-metallicity for  $\text{Co}_2\text{MnAl}$  while the Ga-compounds present deviations. The spin-moment of the Cr impurities varies considerably with the concentration and this behavior is attributed to the position of the majority  $t_{2g}$   $d$ -electrons with respect to the majority  $e_g$  electrons. Disorder simulated by excess of either the Mn or  $sp$  atoms completely destroys the almost perfect spin-polarization of the perfect compounds. It seems that  $\text{Co}_2\text{MnAl}$  and  $\text{Co}_2\text{MnGa}$  compounds are less adequate than the  $\text{Co}_2\text{MnSi}$ ,  $\text{Co}_2\text{MnGe}$  and  $\text{Co}_2\text{MnSn}$  alloys for realistic spintronic applications.

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<sup>1</sup> R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, Phys. Rev. Lett. **50**, 2024 (1983).

<sup>2</sup> Half-metallic alloys: fundamentals and applications, Eds.: I. Galanakis and P. H. Dederichs, Lecture notes in Physics vol. 676 (Berlin Heidelberg: Springer 2005).

<sup>3</sup> A. Bergmann, J. Grabis, B. P. Toperverg, V. Leiner, M. Wolff, H. Zabel, and K. Westerholt, Phys. Rev. B **72**, 214403 (2005); J. Grabis, A. Bergmann, A. Nefedov, K. Westerholt, and H. Zabel, Phys. Rev. B **72**, 024437 (2005); *idem*, Phys. Rev. B **72**, 024438 (2005).

<sup>4</sup> S. Kämmerer, A. Thomas, A. Hütten, and G. Reiss, Appl. Phys. Lett. **85**, 79 (2004); J. Schmalhorst, S. Kämmerer, M. Sacher, G. Reiss, A. Hütten, and A. Scholl, Phys. Rev. B **70**, 024426 (2004).

<sup>5</sup> Y. Sakuraba, J. Nakata, M. Oogane, H. Kubota, Y. Ando, A. Sakuma, and T. Miyazaki, Jpn. J. Appl. Phys. **44**, L1100 (2005).

<sup>6</sup> X. Y. Dong, C. Adelman, J. Q. Xie, C. J. Palmström, X. Lou, J. Strand, P. A. Crowell, J.-P. Barnes, and A. K. Petford-Long, Appl. Phys. Lett. **86**, 102107 (2005).

<sup>7</sup> I. Galanakis, Ph. Mavropoulos, and P. H. Dederichs, J. Phys. D: Appl. Phys. **39**, 765 (2006); I. Galanakis, P. H.

Dederichs, and N. Papanikolaou, Phys. Rev. B **66**, 174429 (2002).

<sup>8</sup> E. Şaşıoğlu, L. M. Sandratskii, P. Bruno, and I. Galanakis, Phys. Rev. B **72**, 184415 (2005).

<sup>9</sup> J. J. Attema, G. A. de Wijs, and R. A. de Groot, J. Phys. D: Appl. Phys. **39**, 793 (2006); K. Nagao, Y. Miura, and M. Shirai, Phys. Rev. B **73**, 104447 (2006); I. Galanakis, M. Ležaić, G. Bihlmayer, and S. Blügel, Phys. Rev. B **71**, 214431 (2005); I. Galanakis, J. Phys.: Condens. Matter, **16**, 8007 (2004).

<sup>10</sup> L. Chioncel, E. Arrigoni, M. I. Katsnelson, and A. I. Lichtenstein, Phys. Rev. Lett. **96**, 137203 (2006); L. Chioncel, M. I. Katsnelson, R. A. de Groot, and A. I. Lichtenstein, Phys. Rev. B **68**, 144425 (2003).

<sup>11</sup> M. Ležaić, Ph. Mavropoulos, J. Enkovaara, G. Bihlmayer, and S. Blügel, Phys. Rev. Lett. **97**, 026404 (2006).

<sup>12</sup> R. Skomski and P. A. Dowben, Europhys. Lett. **58**, 544 (2002).

<sup>13</sup> I. Galanakis, K. Özdoğan, B. Aktaş, and E. Şaşıoğlu, Appl. Phys. Lett. **89**, 042502 (2006).

<sup>14</sup> K. Koepf and H. Eschrig, Phys. Rev. B **59**, 3174 (1999); K. Koepf, B. Velicky, R. Hayn, and H. Eschrig, Phys. Rev. B **58**, 6944 (1998).

<sup>15</sup> I. Galanakis, J. Phys.: Condens. Matter **16**, 3089 (2004).